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In the Application of

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Johannes Wilhelmus Maria Sonnemans et al. Examiner: Tam M. Nguyen

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For: PROCESS FOR EFFECTING ULTRA-DEEP HDS OF HYDROCARBON  
FEEDSTOCKS

**Declaration under 37 C.F.R. §1.132**

Sir:

I, Frans Lodewijk Plantenga, a citizen of the Netherlands, hereby declare and state:

1. I have a Ph.D. in Physical Chemistry which was conferred upon me by the University of Leiden in Leiden, The Netherlands in 1982.
2. I have been employed by Akzo Nobel since 1980 and I have a total of 23 years of work and research experience in the field of refining catalysts. I am presently employed as WW Development Manager Hydroprocessing Catalysts
3. I am one of the inventors of the present application.

I herewith declare as follows:

In recent years, the requirements as to the sulfur content of, in particular, diesel fuel, have become more and more stringent. Up to 2000 the sulfur content of diesel feeds was allowed to be as high as 1500 ppm, and conventional hydrodesulfurisation was sufficient to reach this value. In conventional hydrodesulfurisation the sulfur content of a feedstock is reduced from a value of between 0.5 and 2 wt.% to a value of about 0.15 wt.% (1500 ppm). The compounds converted in conventional hydrodesulfurisation are the relatively easily converted sulfides, disulfides, thiophanes, and benzothiophenes.

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However, with increasingly strict environmental regulations, the maximum amount of sulfur allowable in diesel product decreased to a value of below 200 ppm, and further to a value of below 50 ppm. Therefore, there came a need for a process to further reduce the sulfur content of low-sulfur materials. More in particular, the need arose to reduce the sulfur content of hydrocarbon feeds from a value of below 500 ppm to a value below 200 ppm, preferably below 50 ppm.

Since it is the aim of the petroleum refiner to produce product meeting the minimum required specifications for the lowest possible costs (that is, under the least severe operating conditions), the sulfur level of the products produced in conventional HDS generally was just below the maximum level allowed. There thus was no commercial experience in producing diesel feeds with a sulfur content below 200 ppm, preferably below 50 ppm.

Thus, developing processes for ultra-deep HDS was uncharted territory, and it turned out to be a less straightforward course than expected. Feeds with a sulfur content below 500 ppm generally are feeds which have already been subjected to a hydrodesulfurisation step. In this first step, the reactive sulfur containing compounds, viz., the sulfides and disulfides, have already been removed, followed by the thiophenes and benzothiophenes. The sulfur compounds present in feeds with a sulfur content of below 500 ppm are mainly made up of dibenzothiophenes, more in particular dialkyldibenzothiophenes, which are very stable, non-reactive compounds. As a matter of thermodynamics it is always more difficult to remove a compound present in a low concentration as compared to a compound present in a higher concentration. In the case of removing sulfur from hydrocarbon feeds, this effect is compounded by the situation discussed above, namely that all "easy" compounds have already been removed, leaving only the very hardest to be handled.

(Reference is made to A. Amorelli et al., "Characterisation of sulfur compounds in middle distillates and deeply hydrotreated products", Akzo Catalyst symposium 1991. See page 49, the two sentences beneath the drawings, page 57, the paragraph beneath the drawings, the paragraph on page 59, page 60, last paragraph).

This effect is summarised in the following table, derived from T. Tippet et al., "Ultra low sulfur diesel: Catalyst and Process options" 1998 NPRA. This table shows the necessary increase in catalyst activity to go from 500 ppm product sulfur to 350 ppm, 200 ppm, and 50 ppm at constant reaction temperature.

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product sulfur (wppm)	required catalyst activity (at constant temperature and space velocity, 500 wppm case is set at 100)
500	100
350	130
200	200
50	625

It appears that if the catalyst activity necessary to obtain a sulfur content of 500 ppm is set at 100 and the reaction conditions remain the same, the catalyst activity would have to increase to 200 to obtain a product sulfur content of 200 ppm, and to 625 to obtain a product sulfur content of 50 ppm. In conclusion, the requirements placed on ultra-deep HDS catalysts are very high indeed.

When conventional hydrodesulfurisation catalysts were used in looking for catalysts which could effect this removal of "hard" sulfur-containing compounds, a surprising discovery was made. It appeared that the activity ranking for ultra-deep HDS differed from the activity ranking known for conventional HDS. In other words, the catalysts with the best performance in conventional HDS did not show the best performance in ultra-deep HDS. For example, in conventional HDS, cobalt-molybdenum catalysts are more active than nickel-molybdenum catalysts. However, in ultra-deep HDS it appeared that nickel-molybdenum catalysts are more active than cobalt-molybdenum catalysts. It appeared that while conventional hydrodesulfurisation mainly takes place via direct sulfur removal from the organic molecule, ultra-deep hydrodesulfurisation mainly takes place via a hydrogenation reaction followed by sulfur removal.

(See Xiaoliang Ma et al., "Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel Fuel", Ind. Eng. Chem. Res., 1994, 33, 218-222, in particular page 221, left-hand column, last two paragraphs, and page 221, right-hand column, second paragraph. See also Tippet, "Ultra low sulfur diesel: Catalyst and Process options" 1999 NPRA, the paragraph bridging pages 7 and 8. )

Thus, in summary,

- the requirements to be met by an ultra-deep HDS catalyst are severe
- the materials to be converted in ultra-deep HDS differ from those converted in conventional HDS
- the reaction mechanisms for ultra-deep HDS differ from those for conventional HDS
- the best catalyst ranking differs for conventional HDS and ultra-deep HDS

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The following table summarises the key differences between conventional hydrodesulfurisation (HDS) and ultra-deep HDS.

	conventional HDS	ultra-deep HDS
S content of feed	around 0.5-2 wt. % (20 000 – 80 000 ppm)	less than 500 ppm
S-content of product	about 0.2 wt % (2000 ppm)	below 200 ppm, preferably below 50 ppm
Main compounds to be converted	sulfides, disulfides, thiophenes, benzothiophenes	alkylated dibenzothiophenes
Reaction mechanism	direct S-extraction	hydrogenation followed by S-extraction

Accordingly, conventional HDS and ultra-deep HDS have little more in common than the name. Due to the difference in the nature of the compound to be converted and the nature of the reaction mechanism, there is no way in which a skilled person wishing to develop an ultra-deep HDS process will turn to a catalyst known for its good results in conventional HDS. In fact, when in the process of developing a catalyst suitable for ultra-deep HDS we tested the present HDS catalyst, we merely did so to obtain a starting value for further development. We were highly surprised when it appeared that the catalyst in question actually showed good activity in ultra-deep HDS.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: February 26<sup>th</sup>, 2003

F.J. Plantenga

